l_{co}/L similar to the value obtained for penetrating light. Furthermore, we find that the voltage dependence of η at intermediate wavelengths also follows Eq. (1) but the values of l_{co}/L required to fit the equation are higher than at the blue and red end of the spectrum. We have therefore adopted a simple phenomenological model in which the voltage dependence of η follows Eq. (1), independent of wavelength. This permits us to calculate FF on the basis of the measured l_{co}/L for penetrating light, leading to curve 2 which fits the experimental data quite well. A more exact calculation is not justified at this time, since l_c would have to be measured at many wavelengths, the experimental fit to FF would not be substantially better, and a simple and satisfactory theory for the wavelength dependence of l_c is not available. Curve 2 lies above the averaged experimental curve by a constant amount Δ FF = 0.04. Series resistance will reduce the measured FF from the value predicted from the l_{co}/L measurement, which does not include this effect. For the cells used in this experiment a sheet resistance of 40 $\Omega/\square$ for the CTO layer would bring curve 2 into agreement with the experimental data.

We have shown that a measurement of a single physical quantity, namely, the collection length is sufficient to predict the fill factor. Comparison between measured and predicted fill factors demonstrates that it is the sum of the mobility-lifetime products for both carriers that determines the fill factor rather than the dark current as in single crystal cells. In a forthcoming paper we will show that l_{co}/L as measured above correlates very well with measurements of the diffusion length by means of the surface photovoltage technique. From the data in Fig. 2 we conclude that the majority of cells have fill factors in the range 0.55–0.72 corresponding to $\bar{\mu}\bar{\tau}$ products in the range 1×10^{-8}–6×10^{-8} cm^2/V.

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[1] I. Chen and J. Mort, in *Tetrahedrally Bonded Amorphous Semiconductors*, AIP Conf. Proc. No. 73 edited by R. A. Street, D. K. Biegelsen, and J. C. Knights (AIP, New York, 1981), p. 302.
[2] G. Swartz, J. Appl. Phys. **53**, 712 (1982).
[3] M. Hack and M. Shar, XVI IEEE Photovoltaic Specialists Conference, Sept. 27–30, 1982, San Diego, CA, pp. 1429–30.
[4] R. O. Bell, Appl. Phys. Lett. **36**, 936 (1980).
[5] H. Miyamoto, M. Konagai, and K. Takahashi, Jpn. J. Appl. Phys. **20**, 1691 (1981).
[6] A. Delahoy and R. W. Griffith, J. Appl. Phys. **52**, 6337 (1981).
[7] D. Gutkowicz-Krusin, C. R. Wronski, and T. Tiedje, Appl. Phys. Lett. **38**, 87 (1981); D. Gutkowicz-Krusin, J. Appl. Phys. **52**, 5370 (1981).
[8] V. Dalal and F. Alvares, J. Phys. Paris C **4**, C4-491, (1981); V. Dalal, Solar Cells **2**, 261 (1980).
[9] R. S. Crandall, J. Appl. Phys. **53**, 3350 (1982); R. S. Crandall, RCA Rev. **42**, 449 (1981).
[10] J. Reichman, Appl. Phys. Lett. **38**, 251 (1981).
[11] R. S. Crandall (unpublished).

7.2% efficient polycrystalline silicon photoelectrode

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After etching, *n*-type cast polycrystalline silicon photoanodes immersed in a solution of methanol and a substituted ferrocene reagent exhibit photoelectrode efficiencies of 7.2% ± 0.7% under simulated AM2 illumination. Scanning laser spot data indicate that the grain boundaries are active; however, the semiconductor/liquid contact does not display the severe shunting effects which are observed at a polycrystalline Si/Pt Schottky barrier. Evidence for an interfacial oxide on the operating polycrystalline Si photoanode is presented. Some losses in short circuit current can be ascribed to bulk semiconductor properties; however, despite these losses, photoanodes fabricated from polycrystalline substrates exhibit efficiencies comparable to those of single crystal material. Two major conclusions of our studies are that improved photoelectrode behavior in the polycrystalline silicon/methanol system will primarily result from changes in bulk electrode properties and from grain boundary passivation, and that Fermi level pinning by surface states does not prevent the design of efficient silicon-based liquid junctions.

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We report the first efficient semiconductor/liquid junction based on polycrystalline silicon substrates. Liquid contacts to polycrystalline materials possess intrinsic advantages over solid state contacts.[1] In aqueous systems, polycrystalline substrates have yielded efficiencies approaching those of single crystal material[2–4]; however, for several materials, including *n*-type Si, anode instability pre-

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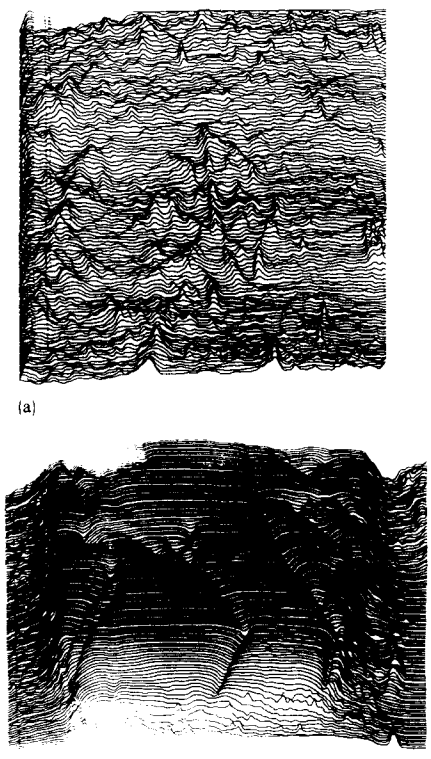
cludes direct study of the semiconductor/liquid interface. Nonaqueous solvent systems are attractive because they provide a rational strategy for the suppression of photocorrosion and photopassivation reactions.[5,6] We recently reported that n-type single crystal Si photoanodes in CH_3OH solvent are capable of stable 10% solar-to-electrical conversion efficiencies under AM2 illumination.[7] Our success with this system has prompted an investigation of liquid junctions formed with technologically important polycrystalline Si.

Samples of cast n-type polycrystalline Si with columnar grain structure (Wacker Siltronic) were cut from 4-in. square slices. The sample size was typically 16 mm^2 which was large enough to contain several tens of grains whose linear dimensions were 100 to 500 μm. Samples were etched to a shiny finish in HNO_3:CH_3COOH:HF (10:4:1) for 40 min at room temperature. Ohmic contacts to the backsides of the samples were formed either with a standard (950 °C) phosphorus predeposition followed by an Al evaporation or with Ga-In eutectic. Other experimental procedures have been described previously.[7] In all experiments a three-electrode cell was employed, and the solution consisted of methanol containing 0.15 M dimethylferrocene, I, 0.5 mM dimethylferricenium, I^+, and 1.5 M $LiClO_4$. All photoelectrode efficiencies were measured using a 0.2-mm outer diameter Luggin probe connected to a Pt wire reference electrode. This configuration minimizes the effects of uncompensated Ohmic resistance on the current-voltage curves.[7] For scanning laser spot (SLS) and spectral response experiments the Luggin probe was not used. The SLS apparatus employed a 5-mW He-Ne laser which was focused to a spot size of 20–40 μm. 2-mm-diam



(a)

(b)

FIG. 1. (a) Scanning laser spot image of a polycrystalline Si anode (etched with 48% aqueous HF) in methanol solution. (b) Scanning laser spot image of the same anode after etching with HNO_3:CH_3COOH:HF (10:4:1) to remove saw damage on surface. Both scans are of a 4×4 mm sample.

Schottky barriers were formed by filament evaporation of nominally 80 Å layers of Pt. All efficiency measurements were made with an ELH-type tungsten-halogen bulb calibrated with a Solarex silicon secondary standard, and no corrections for solution absorption or optical reflection were included.

In Figs. 1(a) and 1(b) we present SLS images (spatial short circuit current response) obtained on a particular sample before and after the HNO_3:CH_3COOH:HF etch treatment. Before etching, grain structures which correspond to those visible in an optical photograph of the surface are not apparent in the SLS image; however, after treatment the structures appear. Thus, surface damage in the as-received samples is so extensive that it obscures the effects of the grain boundaries. Other researchers have reported dramatic increases in the short circuit current of Al Schottky barriers on p-type Wacker polycrystalline Si after similar etch treatments, and have postulated that the removal of a saw-damaged surface layer is responsible.[8] Our data are consistent with their findings, and we may further conclude that, in the case of n-type Wacker polycrystalline Si, grain boundaries remain active after the HNO_3:CH_3COOH:HF etch treatment.

The current-voltage characteristics (70 mW/cm^2 ELH irradiation) of cast polycrystalline Si photoelectrodes in 0.15 M I/0.5 mM I^+/1.5 M $LiClO_4$/CH_3OH are depicted in Fig. 2. Surfaces which were etched only with 48% HF yielded poor current-voltage parameters, and exhibited an open circuit voltage which is nearly a dead short (0.05 V). Prolonged treatment with the HNO_3:CH_3COOH:HF etch removed surface cutting damage, and yielded photoelectrodes with open circuit voltages of 0.51–0.53 V, short circuit current densities of 16–20 mA/cm^2, fill factors of 0.52–0.60, and photoelectrode efficiencies for conversion of light to electric-

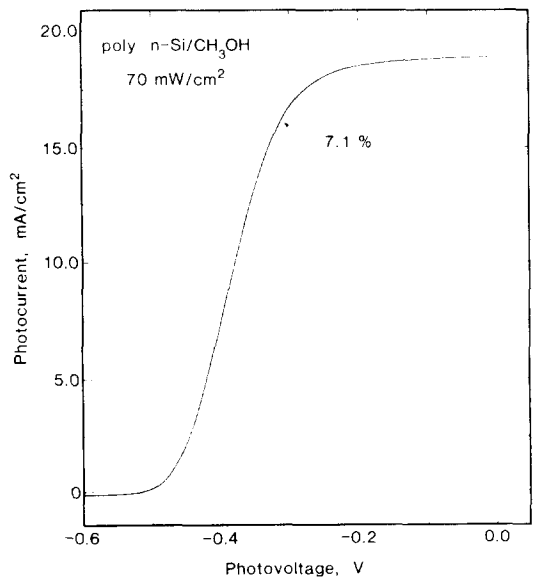


FIG. 2. Current-voltage properties of cast polycrystalline Si photoanodes in methanol solution. The electrolyte is 1.5 M $LiClO_4$, and the redox couple is 0.15 M dimethylferrocene/0.5 mM dimethylferricenium. Light intensity is 70 mW/cm^2 from an ELH-type tungsten-halogen source. Current-voltage properties are measured potentiostatically (50 mV/s) vs a Pt reference electrode through a Luggin capillary, and represent photoelectrode efficiencies of the semiconductor anode. The cathodic current is minimal in these scans due to the low concentration of solution oxidant.

ity of 7.2% ± 0.5%. These values are within 20% of the 8.5% ± 0.5% value obtained for polished single crystal Si surfaces under identical conditions.[9]

In contrast to the characteristics of polycrystalline Si liquid junctions, Pt Schottky barrier devices show near dead shorts even when the Pt is deposited after the HNO_3:CH_3COOH:HF treatment. In view of the large grain size in the cast Si samples, and the fact that identical etching procedures produce rectifying Pt Schottky barriers on single crystal Si surfaces,[7] we attribute the poor device properties of the polycrystalline Si/Schottky barriers to the shunting effect of grain boundaries. Grain boundaries may degrade cell performance either by promoting minority-carrier recombination or by acting as low impedance channels for majority carriers. The improved behavior of the liquid junction system is likely attributable to a reduction in both of these effects. In a liquid, majority-carrier transport between grains is sensitive to the resistivity of the supporting electrolyte, to the mobilities and concentrations of the redox species in solution,[10] and to the physical size of the exposed area of the grain boundary. Thus, the magnitude of the shunt current may be limited by diffusive molecular processes, and even a low value for the solution resistivity may not produce deleterious shunting by majority carriers.

We have also obtained evidence that formation of a surface oxide contributes to the performance of the polycrystalline Si/CH_3OH junction by reduction of surface recombination processes. We have previously reported that Pt barriers formed on single crystal Si which was first immersed in an operating liquid junction cell show a dramatic increase in conversion efficiency compared to conventional Si/Pt barriers.[7] Similar experiments using polycrystalline Si samples also yield an improvement in Schottky barrier cell parameters (V_{oc} = 0.2–0.45 V at J_{sc} = 15 mA/cm^2). These experiments imply that the reduction of surface recombination is an important feature of the methanol/ferrocene electrolyte system. The improvement in the Schottky cells varies considerably from sample to sample, whereas in the liquid junction cells there is little variation (V_{oc} = 0.51–0.53 V). We assume that differences in the number of grain boundaries covered by the metal contacts are responsible for the variation in open circuit voltage. It is attractive to conclude the liquid junction systems are inherently less sensitive than Schottky barrier systems to variations in grain boundary density. However, the Schottky results do indicate an important role for surface silicon oxides in both liquid and Schottky systems.

The observation that the open circuit voltage of the Si/liquid interface is relatively large when compared to typical values for Si/Pt Schottky barriers implies that surface state pinning of the Fermi level does not play a major role in determining the voltage at the Si/methanol interface. Furthermore, a plot of the short circuit photocurrent versus incident light energy is linear for light intensities of 1.0–70 mW/cm^2; thus, such plots do not exhibit saturation effects which might imply the presence of surface recombination states. The photocurrent densities of our polycrystalline Si/liquid junctions are, however, somewhat lower than the theoretical values for single crystal Si cells in our irradiation conditions,[7] and one source of the current loss appears to be in the bulk properties of the material itself. Spectral response data indicate that the quantum efficiencies of polycrystalline and single crystal Si photoelectrodes are comparable in the high-energy region of the spectrum, but the quantum efficiencies of the polycrystalline photoelectrodes decline more rapidly with decreasing photon energy. This decline is indicative of bulk recombination losses in the polycrystalline Si which have a strong effect on deeply penetrating, low-energy photons, and implies that bulk gettering to increase carrier lifetime may yield even higher efficiencies than observed at present.

In conclusion, our studies demonstrate the first efficient polycrystalline silicon/liquid junction. We have shown that the overwhelming effect of shunting grain boundaries on the current-voltage characteristics of solid state devices can be effectively minimized in appropriately designed semiconductor/liquid junction devices. In contrast to recent generalizations which propose that surface states at small band gap semiconductor/liquid interfaces may preclude formation of efficient junctions in nonaqueous solvents,[11] our studies demonstrate a polycrystalline silicon/liquid junction which is not predominately surface limited. These results have prompted studies of smaller grain size material, as well as methods for grain boundary passivation, which will be described in future reports.

[1] A. Heller, Acc. Chem. Res. **14**, 154 (1981).
[2] A. Heller, B. Miller, S. S. Chu, and Y. T. Lee, J. Am. Chem. Soc. **101**, 7633 (1979).
[3] A. Heller, R. G. Vadimsky, W. D. Johnston, Jr., K. E. Strege, H. J. Leamy, and B. Miller, Conf. Rec. 15th IEEE Photovoltaic Spectroscopy Conference 1981, p. 1422.
[4] B. Miller, A. Heller, M. Robbins, S. Menezes, K. C. Chang, and J. Thomson, Jr., J. Electrochem. Soc. **124**, 1019 (1977); D. Cahen, G. Hodes, J. Manassen, and R. Tenne, Adv. Chem. Ser. **146**, 369 (1981).
[5] M. S. Wrighton, Acc. Chem. Res. **12**, 303 (1979); A. J. Bard and M. S. Wrighton, J. Electrochem. Soc. **124**, 1706 (1977).
[6] C. M. Gronet and N. S. Lewis, Nature **300**, 733 (1983); C. M. Gronet and N. S. Lewis, Appl. Phys. Lett. **43**, 115 (1983).
[7] C. M. Gronet, N. S. Lewis, G. Cogan, and J. Gibbons, Proc. Natl. Acad. Sci. U.S.A. **80**, 1152 (1983).
[8] P. A. Lester, R. Singh, D. Rice, R. N. Pangborn, S. Ashok, and S. J. Fonash, in *Grain Boundaries in Semiconductors*, edited by H. J. Leamy, L. E. Pike, and C. G. Seager, Proceedings of Materials Research Society, Boston, MA 1981 (Elsevier, New York, 1982), p. 191.
[9] Improved control over experimental variables has resulted in efficiencies for shiny single crystal *n*-Si anodes which are approximately 10% higher than reported in Ref. 7. This results primarily from increased short circuit photocurrents on shiny Si anodes.
[10] A. J. Bard and L. F. Faulkner, *Electrochemical Principles* (Wiley, New York, 1982).
[11] A. J. Bard, A. B. Bocarsly, F. R. F. Fan, E. G. Walton, and M. S. Wrighton, J. Am. Chem. Soc. **102**, 3671 (1980); K. D. Legg, A. B. Ellis, J. M. Bolts, and M. S. Wrighton, Proc. Natl. Acad. Sci. **74**, 4116 (1977); A. J. Bard, F. R. F. Fan, A. S. Gioda, G. Nagasubramanian, and H. S. White, Disc. Farad. Soc. **70**, 19 (1980).